of the two nickel–chlorine distances and so may be attributable to the adjacent nickel in the linear chain, again according to fit index ratio,[12] integrated area,[11] and correlation[11] tests. Multiple scattering effects were found to have little effect on the analysis of this minor shell. At the present stage of analysis the angle at chlorine has been refined to ca. 140°, but this is a small component of the total EXAFS and this value is open to some doubt. Other small shells were reproducibly apparent in the Fourier transform of the nickel edge EXAFS of **2**; these seem likely to be due to the chloride counterions between the nickel–chlorine chains.

These results confirm complexes **2** and **4** as mixed-valence materials and offer the first structural details about them. They also demonstrate that EXAFS may be valuably applied to the study of such materials; the results of the experimentally more difficult chlorine SOXAFS (soft X-ray absorption fine structure) data are particularly encouraging. The observation of back-scattering atoms out to ca. 5 Å from the absorbing metal center suggests that EXAFS may be used constructively in conjunction with X-ray powder diffraction to derive considerable detail about the lattice structures of these linear-chain compounds.

Acknowledgment. We wish to thank the SERC for access to the facilities of their Daresbury Laboratory and for support for J.T.G. and Richard Perry for some of the samples.

Supplementary Material Available: X-ray absorption spectra of $[Ni(en)_2Cl_2]Cl$ (Ni K-edge), $[Ni(en)_2Cl_2][Ni(en)_2]Cl_4$ (Ni K-edge), $[Ni\{H_2NCH(Me)CH_2NH_2\}_2Cl_2][Ni\{H_2NCH(Me)CH_2NH_2\}_2]Cl_4$ (Ni K-edge), and $[Ni(en)_2Cl_2][Ni(en)_2]Cl_4$ (Cl K-edge) in graphical and listing forms (36 pages). Ordering information is given on any current masthead page.

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Received July 8, 1988

Synthesis of High-Surface-Area α-$LiAlO_2$

Sir:

We have previously reported the room-temperature synthesis of lithium dialuminate, $[LiAl_2(OH)_6]^+(OH)^-\cdot 2H_2O$, by the imbibition of LiOH into bayerite, $Al(OH)_3$, in the molar ratio of 1:2.[1] Because $[LiAl_2(OH)_6]^+(OH)^-\cdot 2H_2O$ retains the layered structure of bayerite, it can react further with soluble salts in a second salt imbibition step. A material prepared with a Li:Al ratio of 1:1 would be a potential precursor for $LiAlO_2$.

$LiAlO_2$ adopts three different structures, the hexagonal α phase, the orthorhombic β phase, and a tetragonal γ phase. These three polymorphs form under similar reaction conditions, and mixtures of these polymorphs are commonly encountered in syntheses performed below 700 °C.[2] Above this temperature, the α- and β-polymorphs begin to convert to the γ-polymorph. The slow kinetics of this conversion make it difficult to identify the transition temperature, but by 900 °C the transformation is generally complete.

The thermal history of polycrystalline oxide materials plays a significant factor in determining their surface area. Conventional solid-state synthetic methods, which require higher temperature to reach complete reaction, yield products that have been desurfaced through sintering. For example, α-$LiAlO_2$ produced by the reaction of Li_2CO_3 with boehmite (AlO(OH)) at 600 °C for 30 h has a platelike morphology with particle size in the range of 1–25 μm and a surface area of less than 5 m^2/g.[3] The salt imbibition technique we report in this communication yields a stoichiometric 1:1 (Li:Al) precursor. Complete reaction to α-$LiAlO_2$ can be accomplished in the shortest time as well as at the lowest temperature because of the atomic scale mixing of components.

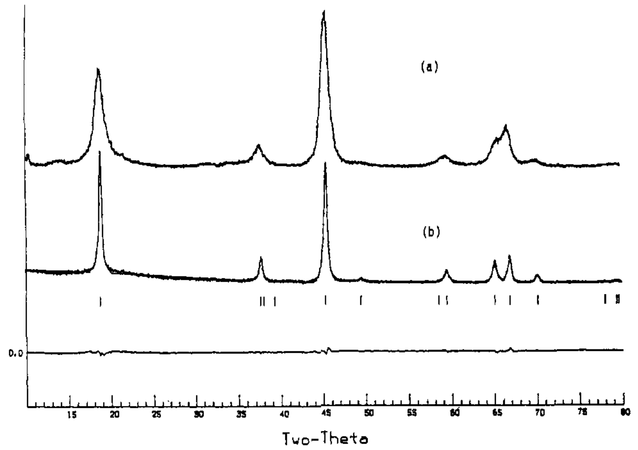

Figure 1. X-ray powder data for lithium monoaluminate calcined at 400 °C for 100 h (a) and refinement profile of polycrystalline α-$LiAlO_2$ (b). In the profile, dots are observed data and the solid line is the best-fit profile. The difference profile appears at the bottom.

Table I. Surface-Area and Pore-Size Data for α-$LiAlO_2$[a]

	SA, m^2/g	PS, Å	MPD, Å	APD, Å	TP, mL/g
400 °C/30 h	68	57	93	99	0.09
500 °C/1 h after 400 °C/30 h	68	59	94	103	0.07
400 °C/100 h	57	65	98	108	0.08
conventional method[b]	<5	138	NA	NA	NA

[a] Abbreviations: SA, specific surface area; PS, particle size; MPD, median pore diameter; APD, average pore diameter; TP, total porosity above 10 Å (radius). [b] Li_2CO_3 and AlO(OH) at 600 °C for 30 h.

The experimental procedure to imbibe $LiOH\cdot H_2O$ into $[LiAl_2(OH)_6]^+(OH)^-\cdot 2H_2O$ was performed by the same methodology as our original synthesis of the dialuminate.[1] Briefly, equimolar amounts of $[LiAl_2(OH)_6]^+(OH)^-\cdot 2H_2O$ and $LiOH\cdot H_2O$ were ground together and then left to react at room temperature under flowing nitrogen gas saturated with water vapor.[4] The product can also be prepared directly by reaction of $Al(OH)_3$ and $LiOH\cdot H_2O$. The reaction product, lithium monoaluminate ($LiAl(OH)_4\cdot nH_2O$; $0.9 \le n \le 1.3$), was identified by X-ray powder diffraction after several hours; however, several days were required for complete reaction. The formula $[LiAl_2(OH)_6]^+[Li(OH)_2\cdot H_2O]^-$ emphasizes that interlayer water of the dialuminate has been replaced by LiOH. No significant amount of an amorphous component was detected. The decomposition behavior of $LiAl(OH)_4\cdot nH_2O$ ($n \approx 1.0$) is very different compared to that of $LiAlO_2\cdot {}^1/_4H_2O$, which has been precipitated[5] from basic aqueous solution. $LiAlO_2\cdot {}^1/_4H_2O$ has an X-ray powder pattern very similar to that of β-$LiAlO_2$ and converts to β-$LiAlO_2$ upon calcination, whereas $LiAl(OH)_4\cdot nH_2O$ ($n \approx 1.0$) converts to α-$LiAlO_2$. Further experimental details will be published separately.

Figure 1 shows the X-ray powder diffraction pattern of α-$LiAlO_2$ prepared at 400 °C for 100 h (curve a), compared with the same material synthesized by the conventional route from Li_2CO_3 and AlO(OH) reacted at 600 °C for 30 h (curve b). In contrast, calcination for 1 h at 500 °C yielded mainly the β-phase. It is noteworthy that β-$LiAlO_2$ remains undetectable at 500 °C if the α-phase is first nucleated with prolonged heating at 400 °C.

The surface area of α-$LiAlO_2$ was studied by the BET method.[6] Median and average pore diameters were calculated by using the

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Table II. Observed and Calculated X-ray Diffraction Data for α-LiAlO$_2$

hkl	d_{cal}, Å	d_{obs}, Å	I_{cal}	I_{obs}
003	4.73	4.75	85.3	84.0
101	2.39	2.40	19.0	18.6
006	2.36	2.37	0.0	0.0
012	2.29	2.30	0.0	0.0
104	2.00	2.01	100.0	100.0
015	1.843	1.845	3.6	3.9
009	1.576	1.577	0.3	0.0
107	1.555	1.555	11.4	11.9
018	1.431	1.431	23.2	22.9
110	1.400	1.399	23.2	23.2
113	1.342	1.341	8.4	8.3
1,0,10	1.224	1.222	0.6	0.6
021	1.208	1.206	1.7	1.8
116	1.204	1.202	0.8	0.8

BJH method.[7] The measurements were done by nitrogen adsorption/desorption with an Omnisorp-360 instrument interfaced with an IBM PC/AT computer, which automatically controlled the experiments followed by data acquisition, reduction, and display. Outgassing at 200 °C for 4 h was performed on each sample before the measurement. The Scherrer equation[8] was employed to obtain the average particle size. Results corresponding to different calcination conditions are shown in Table I. The lithium-based oxide α-LiAlO$_2$ derived from the precursor, LiAl(OH)$_4$·nH$_2$O ($n \approx 1.0$), develops significant surface area and porosity that are stable with time and temperature.

Structural details of α-LiAlO$_2$ have not been improved since an estimate of atomic positions based on X-ray diffraction photographs.[9] Powder data shown in Figure 1b were refined by the Rietveld method.[10,11] The results confirmed that α-LiAlO$_2$ is isostructural with α-NaFeO$_2$ with sheets of alternating LiO$_{6/6}$ and AlO$_{6/6}$ octahedra that result in a superlattice of the NaCl structure elongated along the 3-fold axis ($c/2a_{\text{obsd}} = 2.54$ vs $c/2a_{\text{cubic}} = 2.45$).

Powder data were obtained with Ni-filtered Cu Kα radiation on a Rigaku Geigerflex powder diffractometer over the range $10° \leq 2\theta \leq 80°$ in increments of 0.05°. The structure was determined with the full-matrix least-squares program DBW3.2.[12,13] α-LiAlO$_2$ has the space group $R\bar{3}m$ (No. 166, hexagonal setting) with $a = b = 2.7993$ (5) Å, $c = 14.180$ (3) Å, and $Z = 3$. In the unit cell, lithium and aluminum cations take (3a) and (3b) positions, respectively, while the oxygen anions are in the special position (6c) with $z = 0.2406$ (3). This agrees with the estimated range 0.235–0.240 reported earlier.[9] A pseudo Voigt function, which is the sum of Gaussian and Lorentzian functions with adjustable mixing parameters, was employed for profile fitting. The refinement converged with background and half-width parameters as variables. Final R factors[12,13] were $R_p = 8.82\%$, $R_{wt} = 11.22\%$, and Bragg $R = 1.63\%$ ($R_{ex} = 9.11\%$, $R_{wt}/R_{ex} = 1.23$). Bragg reflections with their relative intensities are given in Table II.

Interatomic distances obtained are in good agreement with those reported in the literature.[9] All metal ions in α-LiAlO$_2$ have coordination number 6 (D_{3d}) with equidistant oxygen neighbors. Bond distances predicted from the ionic radii of Shannon[14] for octahedral Li$^+$, Al^{3+}, and O^{2-} are Li–O = 2.16 Å and Al–O = 1.94 Å, compared well with the observed values 2.084 (1) and 1.926 (1) Å, respectively. In-plane oxygen–oxygen separations corresponding to the a-axis length are 2.799 (1) Å. As expected, there are slightly shorter interplane oxygen–oxygen distances of 2.647 (1) Å for the Al–O sheet with longer 3.087 (1) Å oxygen–oxygen separations in the Li–O sheet.

The compound precursor LiAl(OH)$_4$·nH$_2$O ($n \approx 1.0$) effectively overcomes the intrinsic barrier associated with lithium ion diffusion encountered when lithium salts react with alumina.[15] Decomposition results in high-surface-area α-LiAlO$_2$ because of the short reaction time and relatively low temperature. Future work will explore the use of high-surface-area α-LiAlO$_2$ as a catalyst support and for the preparation of delithiated transitional alumina compounds.[3]

Acknowledgment. This research was supported by the National Science Foundation, Solid State Chemistry (Grant DMR-8610659), and the Alcoa Foundation. We also thank Lorraine A. Townsend for her assistance with the BET/BJH measurements. The purchase of the instrument was made possible by DOE (Contract No. DE-FG05-86ER75295).

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Received April 18, 1988

Dinuclear Mixed Alkyl Phosphido and Alkyl Aryloxy Complexes of Manganese(II). Crystal Structures of [Mn(CH$_2$CMe$_3$)(μ-t-Bu$_2$P)]$_2$ and [Mn(CH$_2$CMe$_2$Ph)(μ-O-2,4,6-(t-Bu)$_3$C$_6$H$_2$)]$_2$

Sir:

Apart from binary (homoleptic) complexes,[1] most phosphido and arsenido (R$_2$E$^-$, E = P, As) complexes of the d-block transition metals also bear stabilizing ligands such as cyclopentadienyl, CO, phosphine, and NR$_2^-$.[2] During the course of our studies on the steric effects of bulky phosphido complexes of the d-block transition metals,[3] we examined reactions of the manganese(II) dialkyls

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